

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **09-092265**

(43)Date of publication of application : **04.04.1997**

(51)Int.Cl.

H01M 4/02

H01M 4/04

H01M 4/58

(21)Application number : **07-244755**

(71)Applicant : **DENSO CORP**

(22)Date of filing : **22.09.1995**

(72)Inventor : **ADACHI NORIKAZU
KOJIMA HISANAO**

(54) POSITIVE ACTIVE MATERIAL OF SECONDARY BATTERY, ITS MANUFACTURE, AND POSITIVE ELECTRODE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive active material for a high performance secondary battery by improving the arranging relation of a metal oxide constituting an active material main body and a carbon material.

SOLUTION: A positive active material of a secondary battery consists of a powdery metal oxide constituting an active material main body and a carbon material which covers 15% or more of the apparent surface of the metal oxide in the thickness of 0.01-0.3 μ m and has a specific surface area of 150m²/g or more. By covering with very thin carbon material layer, ion permeability and conductivity are jointly provided, and high performance is obtained. By mixing a conductive material to the positive active material, a positive electrode with high performance is obtained.

LEGAL STATUS

[Date of request for examination] 27.04.2001

[Date of sending the examiner's decision of rejection] 30.05.2003

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3601124

[Date of registration] 01.10.2004

[Number of appeal against examiner's decision of rejection]	2003-012110
[Date of requesting appeal against examiner's decision of rejection]	27.06.2003
[Date of extinction of right]	

CLAIMS

[Claim(s)]

[Claim 1] The metallic oxide of the shape of powder which constitutes the body of an active material, and positive active material of the rechargeable battery characterized by wrap specific surface area consisting 15% or more on the front face of appearance of this metallic oxide of a carbon material 150m² / more than g by the thickness of 0.01 micrometers - 0.3 micrometers.

[Claim 2] A carbon material is the positive active material of the rechargeable battery according to claim 1 the specific surface area of whose is 250m² / g-1500m² / g.

[Claim 3] A carbon material is the positive active material of the rechargeable battery according to claim 1 which is KETCHIEN black or acetylene black.

[Claim 4] A carbon material is the positive active material of the rechargeable battery of wrap claim 1 publication at the thickness of 0.01 micrometers - 0.2 micrometers about 15% - 80% on the front face of appearance of a metallic oxide.

[Claim 5] Positive active material of the rechargeable battery according to claim 1 whose specific surface area is 3.5m² / g-100m² / g.

[Claim 6] A metallic oxide is the positive active material of the rechargeable battery according to claim 1 which is at least one sort of a lithium manganic acid ghost, a lithium nickel oxide, a lithium ferric acid ghost, lithium cobalt oxide, and manganese oxide.

[Claim 7] The manufacture approach of the rechargeable battery positive active material characterized by applying compression shearing stress to the compounding operation which blends the powder-like metallic oxide and powder-like carbon material which constitute the body of an active material, and this metallic oxide and this carbon material, and consisting 15% or more on the front face of appearance of this metallic oxide of a wrap coat process by the thickness of 0.01 micrometers - 0.3 micrometers in the front face of this metallic oxide with this carbon material.

[Claim 8] The positive electrode of the rechargeable battery characterized by having the binder which binds the carbon powder, this positive active material, and this carbon powder which constitute the electric conduction agent which intervenes between the positive active material with which wrap specific surface area consists of a carbon material 150m² / more than g 15% or more on the front face of appearance of the metallic oxide of the shape of powder which constitutes the body of an active material, and this metallic oxide by the thickness of 0.01 micrometers - 0.3 micrometers, and this positive active material.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to amelioration of the positive active material of the rechargeable battery with which a metallic oxide is used as an active material and a water solution or a nonaqueous solution is used for it as the electrolytic solution.

[0002]

[Description of the Prior Art] Various metallic oxides are used as positive active material of a cell. the many -- a ratio -- since electric conductivity is low, the electric conduction agent is needed. And an electric conduction agent is arranged between metallic-oxide powder, electronic conductivity is given, and the reduction reaction is promoted. The carbon material is used as this electric conduction agent.

[0003] A powder-like metallic oxide, the mixed state of a carbon material, and both arrangement condition pose a problem as one of the factors which affects the property, especially discharge engine performance of a cell. If an arrangement condition is bad and there is a bad conductive part, an electron will not be supplied to the metallic oxide there, but it will be in an unreacted condition, and will not work as an active material. For this reason, there is a problem that the utilization factor of a metallic oxide is low.

[0004] Conversely, if the mixed state of a carbon material is made more into homogeneity, since the original electrochemical potential which a metallic oxide shows will not be obtained but mixed potential with a carbon material will be observed, the circuit potential as a cell falls as a result. Thus, the cell engine performance is greatly influenced by arrangement of a metallic oxide and a carbon material. The positive active material which formed graphite impalpable powder in the particle front face of the manganese dioxide shown in JP,61-214362,A as a layer as what improved the relation between this metallic oxide and a carbon material is proposed. Moreover, the positive active material which set the particle-size ratio of metallic-oxide powder and artificial-graphite powder to 10-1 to 10-5, and made coverage of a wrap carbon material 0.5 - 15% for the metallic oxide is proposed by JP,7-36332,B.

[0005]

[Problem(s) to be Solved by the Invention] This invention also improves the arrangement relation between a metallic oxide and a carbon material, and aims it at development of the positive active material of the rechargeable battery of high performance more.

[0006]

[Means for Solving the Problem] this invention person covered the carbon material on the surface of the metallic oxide, and it tried to obtain the positive active material of high performance by optimizing a coat condition. And a specific carbon material is used, it discovers that the positive active material of high performance can be obtained by making coat thickness of the carbon material very thin, and this invention is completed.

[0007] That is, specific surface area uses the carbon material 150m² / more than g, and the positive active material of the rechargeable battery of this invention is a wrap thing by the thickness of 0.01 micrometers - 0.3 micrometers in the carbon material about 15% or more on the front face of appearance of a metallic oxide. Using a carbon material with a

large specific surface area, by making the layer of a wrap carbon material very thin for a metallic-oxide front face, the conductivity which was excellent as an active material, and the permeability of ion, such as a lithium ion, are raised, and it considers as the active material of high performance in this invention.

[0008] As a metallic oxide used for this invention, metallic oxides, such as a lithium manganic acid ghost, a lithium nickel oxide, a lithium ferric acid ghost, lithium cobalt oxide, and manganese oxide, can be used as usual. The specific surface area of the carbon material used for this invention is a thing 150m^2 / more than g. The thing with a desirable carbon material with a specific surface area high [more than 150m^2 / g, and specific surface area] is because the film of a wrap carbon material serves as porous one and turns into good film of ionic permeability with electronic conductivity in a metallic-oxide front face. In addition, the specific surface area of a more desirable carbon material is the thing of 250m^2 / g- 1500m^2 / g. As a carbon material with such a high specific surface area, acetylene black and KETCHIEN black are good.

[0009] A carbon material covers 15% or more on the front face of appearance of a metallic oxide by the thickness of 0.01 micrometers - 0.3 micrometers. The appearance front face of a metallic oxide means the outside surface of the oxide particle which constitutes metallic-oxide powder here. The inner surface which divides the hole currently formed in the interior of a particle and a crack is not included. a carbon material -- the appearance front face of a metallic oxide -- 15 - 80% is covered preferably 15% or more. When a coat is smaller than 15%, there is little initial capacity of a positive electrode. This is considered to be because for electronic electric conduction not to be carried out to homogeneity. Conversely, since the weight ratio of a carbon material will increase if a coat increases, it is desirably [80% or less of] good.

[0010] Since migration of the lithium ion which lets a coat pass will become slow if it becomes thick, the thickness of a coat of a carbon material has 0.01 micrometers - good 0.3 micrometers. The thickness of a coat of a carbon material has the good range of 0.01 micrometers - 0.2 micrometers, especially in order to satisfy both electronic conductivity and ionic permeability. As for the specific surface area of the metallic oxide which covered the carbon material, i.e., the positive active material of this invention, it is desirable that they are 3.5m^2 / g- 100m^2 / g.

[0011] It is also desirable to mix the binder for forming the graphite powder for preventing the conductive defect by telescopic motion of the active material at the time of charge and discharge further to an active material in addition to the above mentioned metallic oxide and a carbon material and an electrode. It is desirable to adopt the graphite whose particle size is 1 micrometer - 20 micrometers as graphite powder, and the loadings are good to carry out 0.5-8 weight section combination per metallic-oxide 100 weight section. Moreover, PVDF (polyvinylidene fluoride) can be adopted as a binder and the loadings are good to carry out 1-10 weight section combination per metallic-oxide 100 weight section.

[0012] The positive active material of the rechargeable battery of this invention carries out specified quantity combination of the powder-like metallic oxide and powder-like carbon material which constitute the body of an active material, and is obtained by applying compression shearing stress to this compound, and rubbing in a carbon material on the surface of a metallic oxide. The equipment shown in the sectional view of drawing 6 as equipment which applies this compression shearing stress can be used. The coat film

of a 0.01 micrometers - 0.3 micrometers very thin carbon material can be formed in a metallic-oxide front face by rubbing a carbon material into a metallic-oxide front face.
[0013]

[Function] The positive active material of the rechargeable battery of this invention covers very thinly a carbon material with a large specific surface area on the front face of the metallic oxide which forms the body of an active material. Since the coat is formed with the carbon material with a large specific surface area, and since the coat is made very thin with 0.01 micrometers - 0.3 micrometers, a coat serves as the shape of thin porous one, and the permeability of ion, such as a lithium ion, is good. And conductivity is also excellent with the coat of a carbon material. For this reason, it becomes the positive active material of high performance.

[0014]

[Example] Hereafter, an example explains concretely. At this example, it is LiMn 2O₄ to the body of an active material. It used and the positive active material for lithium secondary batteries was manufactured. This LiMn 2O₄ It is what was compounded with the liquid phase process, and that first [an average of] particle size is 1 micrometer, and the second [an average of] particle size is 3 micrometers.

[0015] As a carbon material, the carbon black 9 (mean particle diameter of 0.04 micrometers, specific surface area of 60m² / g) and CF 3050B (mean particle diameter of 0.04 micrometers, specific surface area of 50m² / g) of Mitsubishi Kasei, the acetylene black (mean particle diameter of 0.02 micrometers, specific surface area of 162m² / g) of DENKI KAGAKU KOGYO, and the KETCHIEN black (mean particle diameter of 0.03 micrometers, specific surface area of 1270m² / g) of LION were used.

[0016] LiMn 2O₄ It is LiMn 2O₄ as an approach of covering a carbon material on a front face. Mixed powder which mixed the carbon material was performed using the carbon coat formation equipment shown in drawing 6. The rotating drum 1 in which, as for this carbon coat formation equipment, the diameter of inner circumference has the building envelope 10 200mm and whose shaft-orientations die length are 70mm. The 1st arm 4 with the press shearing head 3 of the semicircle configuration which is fixed to the fixed shaft 2 inside this rotating drum 1, and is prolonged even near the inner skin of a rotating drum 1, A predetermined include angle is separated behind [revolution] this 1st arm 4, and it is fixed to the fixed shaft 2, and consists of the 2nd arm 6 with the pawl 5 prolonged even near the inner skin of a rotating drum 1.

[0017] It is LiMn 2O₄ at ***** by putting said 250g mixed powder into the building envelope 10 of this carbon coat formation equipment, considering the rotational frequency of a rotating drum 1 as a part for /about 2000 times, processing for 30 minutes, applying compression shearing stress between the inner skin of a rotating drum 1, and the press shearing head 3, failing to scratch and mixing by the pawl 5, after that. The carbon material was covered on the front face. This prepared the active material of this invention. (Active material of an example 1) It is said LiMn 2O₄ as a body of an active material. It used and KETCHIEN black was used as a carbon material. And 3 % of the weight of KETCHIEN blacks was mixed to this LiMn₂ O₄ 97% of the weight, the rotational frequency was considered as a part for /about 2000 times with the carbon coat formation equipment which described a part for this mixing above, it processed for 30 minutes, and the active material of this invention was obtained.

[0018] The SEM (scanning electron microscope) photograph of this active material and

the carbon map by Auger-electron-spectroscopy analysis are shown in drawing 7 and drawing 8. By these SEM and carbon maps, it is spherical LiMn 2O4. It can check that the carbon material has covered to homogeneity on a front face.

(Creation of the electrode A using the active material of an example 1) the active material 97 weight section obtained in order to investigate the property of the obtained active material -- receiving -- PVDF (polyvinylidene fluoride) of a binder -- 3 weight sections combination -- carrying out -- further -- the N-methyl-2-pyrrolidone of a solvent -- the 150 weight sections -- in addition, it kneaded and considered as the shape of a paste. And the obtained paste is coated on aluminum foil charge collector with a doctor blade method, and it dries at 80 degrees C after that for 1 hour, and is 2.3 mC/cm. Press molding was performed by the pressure and the electrode A with a thickness of 0.1mm was created.

[0019] This electrode A was pierced to discoid with a diameter of 14mm, the vacuum drying was carried out at 80 more degrees C for 4 hours, it carried in all over the dry box after that, and the carbon button mold cell was manufactured. the solvent which did Celgard 2400 (trade name) of the microporous polypropylene film at Metal Li and the separator, and did each 50 capacity % mixing of 1 M-LiPF₆ / PC(50) DME (50), i.e., PC (propylene carbonate) and DME (dimethoxyethane), at the counter electrode at the electrolytic solution -- LiPF₆ The electrolytic solution which 1-M-dissolved was used.

[0020] Assessment of an electrode was performed as follows. Charge is 2 mA/cm² first. It carried out until it amounted to 4.1V in constant current, and it carried out by the constant voltage of after that 4.1V for a total of 5 hours. Discharge is 2 mA/cm. It carried out until it amounted to 2.0V. x mark and Sign A of drawing 1 show the relation of the positive-electrode capacity of Electrode A and the number of cycles which used the active material of this example 1. The initial capacity of this electrode was as high as 190 mAh/g, the cycle property was also good, and the positive-electrode capacity after 30 cycles showed 165 mAh/g and the high engine performance.

(Creation of the electrode B using the active material of an example 1) The graphite powder 2 weight section of the mean particle diameter of 3.5 micrometers, and specific surface area of 34m² / g was blended as the active material 97 weight section of an example 1, the PVDF3 weight section of a binder, and an electric conduction agent, and Electrode B was further created for the N-methyl-2-pyrrolidone of a solvent by the same approach as the 150 weight sections, in addition an example 1. It is only different that graphite powder is in Electrode A and its presentation by 5 weight *****, and the others of this electrode B are the same as that of Electrode A also including the manufacture approach.

[0021] The relation between the positive-electrode capacity of this electrode B and the number of cycles is doubled with drawing 1, and - mark and Sign B show it. The electrode B which blended and made the graphite powder of an electric conduction agent to the active material of an example 1 excelled further the electrode A with which the electric conduction agent is not blended in the engine performance. The outstanding property that little lowering of positive-electrode capacity which falls as the number of cycles increases especially is shown. I think that this is effective in the graphite powder blended as an electric conduction agent preventing the conductive lack resulting from telescopic motion of the active material at the time of charge and discharge.

In order to compare the engine performance of the conventional active material and the

active material of this invention, (Creation of the electrode C using the conventional active material) Said LiMn 2O₄ which is the body of an active material used in order to obtain the active material of this invention Powder is used as a conventional active material as it is. This LiMn 2O₄ The powder 89 weight section, said graphite powder 8 weight section, the PVDF3 weight section of a binder, and the N-methyl-2-pyrrolidone 150 weight section of a solvent were added and kneaded, and it considered as the paste. And Electrode C was created by the completely same approach as the electrode A which described this paste above, and Electrode B.

[0022] The relation between the positive-electrode capacity of this electrode C and the number of cycles is doubled with drawing 1 , and O mark and Sign C show it. The electrode A created using the active material of this invention and Electrode B have a very large positive-electrode capacity, and there is also little reduction of the capacity accompanying the increment in the number of cycles so that clearly from the positive-electrode capacity of the electrode C created using the conventional active material shown with Sign C.

(Relation of the coverage of the carbon material which covers the body of an active material) In order to investigate the relation of the coverage of the carbon material which covers the body of an active material LiMn 2O₄ described above as a body of an active material The KETCHIEN black described above as powder and a carbon material is used. LiMn 2O₄ The processing time by the blending ratio of coal of powder and KETCHIEN black and the above mentioned carbon coat formation equipment is adjusted, and it is carbon material coverage (the whole outside surface of the body of an active material makes the condition of having been covered with the carbon material 100% of coverage.). Six kinds of different active materials were prepared. And these six kinds of active materials were used, respectively, six kinds of electrodes were prepared by the completely same approach as the above mentioned electrode A, respectively, and an initial capacity of a positive electrode was measured by the same approach. The obtained result is shown in drawing 2 .

[0023] In addition, coverage computed coverage by carrying out the image processing of the carbon map after surface cleaning by Auger-electron-spectroscopy analysis. An initial capacity of a positive electrode falls gradually as an initial capacity of a positive electrode becomes max and coverage increases, when coverage is about 30% so that clearly from drawing 2 . This will be considered for the weight ratio of a carbon material to increase if coverage increases. On the other hand, to about 20% of coverage, an initial capacity of a positive electrode increases quickly as coverage increases. In the result of drawing 2 , an initial capacity of a positive electrode is small at less than 15% of coverage. Moreover, it turns out that an initial high capacity of a positive electrode by which about 20 - 80% of coverage was stabilized is obtained.

(Relation of the coat thickness of the carbon material which covers the body of an active material) It is LiMn 2O₄ like the time of investigating the relation of said coverage. The processing time by the blending ratio of coal of powder and KETCHIEN black and the above mentioned carbon coat formation equipment was adjusted, and coverage prepared the active material which is seven kinds from which the thickness of a carbon material differs at 80% or more. In addition, an active material with a carbon material coat thickness of 0mm is what did not perform processing by carbon coat formation equipment, and is only LiMn 2O₄. It is the thing of only the powder 100 weight section.

Moreover, Auger-electron-spectroscopy analysis of the depth direction by Ar sputter performed coat thickness of a carbon material.

[0024] These seven kinds of active materials were used, respectively, seven kinds of electrodes were prepared by the completely same approach as the above mentioned electrode A, respectively, and an initial capacity of a positive electrode was measured by the same approach. The obtained result is shown in [drawing 3](#) . Even if the thin film of a carbon material with very as thin coat thickness as about 0.01 micrometers is formed so that clearly from [drawing 3](#) , an initial big capacity of a positive electrode is shown. And an initial capacity of a positive electrode falls as coat thickness increases. Practical coat thickness is about 0.01-0.3 micrometers. If this becomes thicker than 0.3 micrometers, it will be considered to be because for migration of the lithium ion which lets a coat pass to become slow. In order to obtain electronic conductivity and ionic permeability, it is judged that it is desirable and the range of 0.01 micrometers - 0.2 micrometers is good. Four kinds of above mentioned carbon black and the above mentioned graphite powder are used. (Relation of the specific surface area of the carbon material which covers the body of an active material) Moreover, the body of an active material is same LiMn 2O4 as having used it in the example. Powder is used. LiMn 2O4 The processing time by the blending ratio of coal of powder and each carbon material and the above mentioned carbon coat formation equipment was adjusted, and the coverage of a carbon material prepared the active material which is five kinds from which the specific surface whose coat thickness is about 0.1 micrometers at about 60% differs.

[0025] These five kinds of active materials were used, respectively, five kinds of electrodes were prepared by the completely same approach as the above mentioned electrode A, respectively, and an initial capacity of a positive electrode was measured by the same approach. The obtained result is shown in [drawing 4](#) . More than 150m² / g of the specific surface area of a carbon material are good so that clearly from [drawing 4](#) . Capacity improves further by making it desirable 250m² / more than g.

[0026] As an ingredient which fills this, acetylene black and KETCHIEN black are good. A coat will become porous [-like] and this reason will be considered that the penetrable good film of ion also with sufficient electronic conductivity is from formation ***** , if an ingredient with a large specific surface area is used.

(Relation of the specific surface area of an active material) LiMn 2O4 from which six kinds of particle size differs in order to investigate the relation of the metallic oxide which covered the carbon material, i.e., the specific surface area of ***** and an initial capacity of a positive electrode, Powder was prepared. And each LiMn 2O4 Powder and said KETCHIEN black were used, the processing time by the blending ratio of coal and the above mentioned carbon coat formation equipment was adjusted, and the coverage of a carbon material prepared the active material which is six kinds from which the specific surface whose coat thickness is about 0.1 micrometers at about 60% differs.

[0027] These six kinds of active materials were used, respectively, six kinds of electrodes were prepared by the completely same approach as the above mentioned electrode A, respectively, and an initial capacity of a positive electrode was measured by the same approach. The obtained result is shown in [drawing 5](#) . The specific surface area of an active material has good 3.5m² / g-100m² / g so that more clearly than [drawing 5](#) . In this case, since the reinforcement of an electrode will fall if specific surface area makes it larger than 100m² / g, the active material of this range is good.

[0028]

[Effect of the Invention] An initial capacity of a positive electrode of the positive active material of the rechargeable battery of this invention is large, and even if an activity cycle increases, there is little lowering of positive-electrode capacity. Thus, the positive active material of the rechargeable battery of this invention is the thing of high performance. Moreover, the active material of this invention can apply compression shearing stress for the powder-like metallic oxide and powder-like carbon material which constitute the body of an active material, can manufacture it by rubbing a carbon material on the surface of a metallic oxide, and can be manufactured easily.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the charge-and-discharge cycle of an electrode and the relation of positive-electrode capacity which were obtained using the active material and the conventional active material of an example.

[Drawing 2] It is drawing showing the relation of the coverage of a carbon material and an initial capacity of a positive electrode which constitute an active material.

[Drawing 3] It is drawing showing the relation of the coat thickness of a carbon material and an initial capacity of a positive electrode which constitute an active material.

[Drawing 4] It is drawing showing the relation of the specific surface area of a carbon material and an initial capacity of a positive electrode which constitute an active material.

[Drawing 5] It is drawing showing the relation between the specific surface area of an active material, and an initial capacity of a positive electrode.

[Drawing 6] It is the outline sectional view of the carbon coat formation equipment used in the example.

[Drawing 7] It is the SEM image in which the particulate structure of an active material with the carbon material coat of an example is shown.

[Drawing 8] It is Auger-electron-spectroscopy analysis drawing showing the carbon abundance (carbon drawing) of the particulate structure of the active material of drawing 7.

[Description of Notations]

1 -- Rotating drum 2 -- Fixed shaft

3 -- Press shearing head 4 -- The 1st arm 4

5 -- Pawl 6 -- The 2nd arm
